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The potential of lignocellulosic ethanol production in the Mediterranean Basin

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ABSTRACT

This review provides an overview of the potential of bioethanol fuel production from lignocellulosic residues in the Mediterranean Basin. Residues from cereal crops, olive trees, and tomato and grape processing are abundant lignocellulosic wastes in France, Italy, Spain, Turkey and Egypt, where their use as raw materials for ethanol production could give rise to a potential production capacity of 13 Mtoe of ethanol. Due to the lack of sufficient amounts of agricultural residues in all of the other Mediterranean countries, use of the cellulosic content of municipal solid waste (MSW) as feedstock for ethanol fuel production is also proposed. A maximum potential production capacity of 30 Mtoe of ethanol could be achieved from 50% of the 180 million tons of waste currently produced annually in the Mediterranean Basin, the management of which has become a subject of serious concern. However, to make large-scale ethanol production from agricultural residues and MSW a medium-term feasible goal in the Mediterranean Basin, huge efforts are needed to achieve the required progress in cellulose ethanol technologies and to overcome several foreseeable constraints.

Contents

1. Introduction

The world's increasing energy demand and continued use of fossil fuels is the subject of rising concern for the security of the oil supply, as evidenced by increasing oil prices, which peaked at $147.30 per barrel in July 2008 [1]. The combustion of fossil fuels

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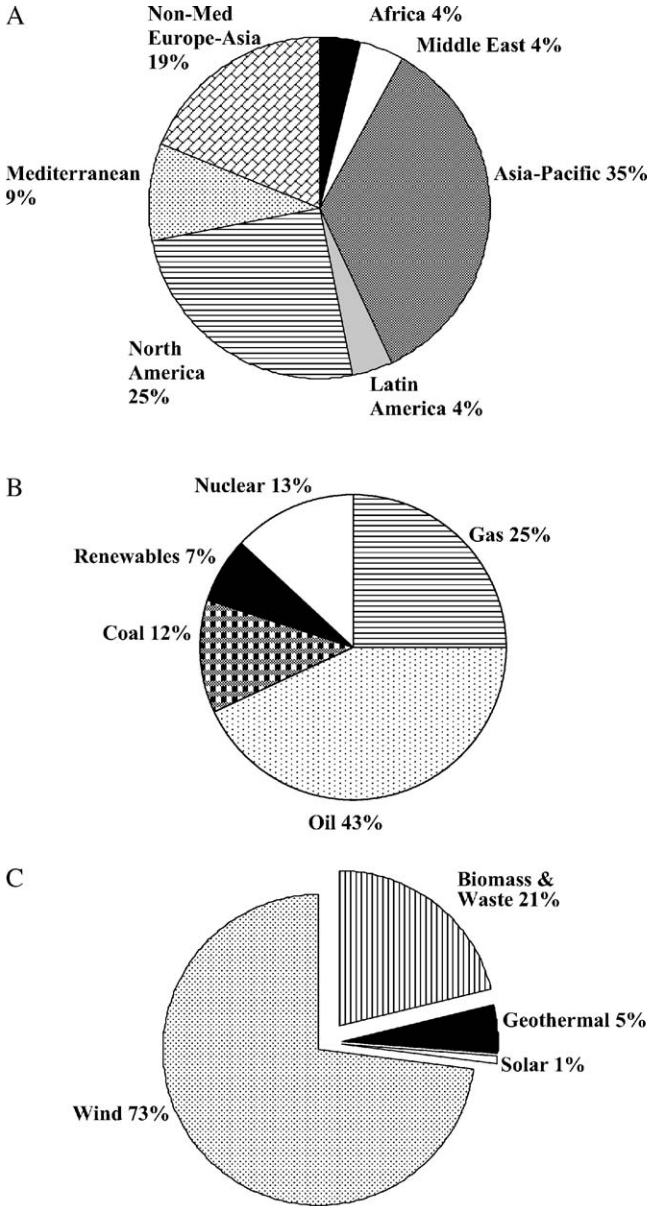

Fig. 1. (A) World total energy demand in 2005. (B) Energy demand in the Mediterranean in 2005. (C) Renewable capacity in the Mediterranean in 2005. RES: renewable energy sources. Data were obtained from OME (2009) at: www.ome.org.

is responsible for 73% of the world's CO_2 production [2], creating alarm over global warming [3,4].

Demand for energy in the Mediterranean has more than doubled in the last 30 years [5], due to population growth and economic development. The Mediterranean Basin covers portions of three continents: Europe, with the Iberian Peninsula, Italian Peninsula, and Balkan Peninsula; western Asia, with the western and southern portions of the peninsula of Anatolia, and Africa, with the northern portion of the Maghreb region of northwestern Africa. Despite its unique natural resources, this region is threatened by climatic change and by a growing demand for energy that exceeds available sources, including fossil fuels [6]. The almost half a billion people living in the Mediterranean Basin currently consume 990 Mtoe of energy, accounting for about 9% of the world's energy demand (Fig. 1A) [7].

The Mediterranean has enormous potential for both conventional and renewable energy production. This region holds 4.6% of the world's proven oil and gas reserves (61.5 billion barrels), almost all (94%) located in Libya (which alone holds over two thirds), Algeria and Egypt. Although most of the countries in the Mediterranean have been thoroughly explored for hydrocarbons, those in the southwest Mediterranean are still under-explored.

As for the renewable energy capacity installed in the Mediterranean, although showing remarkable progress with non-hydro renewable resources over the last 30 years, at an average annual growth rate of 26%, these resources satisfied only 7% of the Mediterranean's primary energy demand in 2005 (Fig. 1B). Most of the non-hydro renewable capacity installed in 2005 (19 GW) was due to wind-power capacity, which reached 14 GW in 2005 from only 3 GW in 2000 (Fig. 1C). The northern Mediterranean countries are the largest renewable energy producers in the region, accounting for over 70% of renewable capacity-based electricity generation in 2005. However, continued deployment of renewable energy production is taking place in the southern Mediterranean countries, especially Turkey and Egypt.

Energy utilization in the Mediterranean is rapidly growing and the use of non-fossil energy sources is becoming critical. Currently, renewable energy resources in the Mediterranean are not efficiently utilized, and there is under-exploitation of biomass for biofuel production to meet energy needs, biomass accounting for just 21% of the total renewable capacity in 2005 (Fig. 1C). More research and development on renewable energy production are therefore absolutely required for the Mediterranean region.

Globally, there is great interest in finding renewable fuels to replace petroleum-based ones, with the dual purpose of enhancing energy security and mitigating climate change, and the biofuels ethanol and biodiesel are potential options for meeting these needs in the transportation sector [8]. The uniqueness of cellulosic ethanol as a sustainable liquid transportation fuel, which can be produced in high volumes and at low cost, and its many powerful benefits, have been recognized for decades [9–13]. A recent awareness of the urgent need to advance cellulosic ethanol production is evidenced by the number of reviews reported on the theme of ethanol fuel production from lignocellulosic biomass, with great attention to ethanol production from lignocellulosic residues, such as crop and wood residues and municipal solid waste (MSW) [14–21].

Identifying lignocellulosic residues for use as raw materials in the effective large-scale production of bioethanol fuel in the Mediterranean is an urgent priority in order to meet growing energy demand and to counteract the dramatic increase in heat-stress risk occurring in the region [22]. As a step in this direction, this paper provides an overview of potential of bioethanol fuel production from lignocellulosic residues in the Mediterranean. The small extent of forest lands in Mediterranean countries, where only 9% of the total land area is used for forestry [23], and the resultant low diffusion of the wood industry, cause less production of wood residues that could be used as raw materials for biofuel production in comparison to countries such as Sweden, Canada and the USA, where much of the available lignocellulose biomass is softwood. As an alternative, the feasibility of ethanol production from crop residues and MSW in the Mediterranean is analyzed.

2. Importance of biofuel energy for the Mediterranean

The energy demand in the Mediterranean is expected to increase by an average 1.5% per year, reaching up to 1426 Mtoe by 2030 (Fig. 2). Most of this increase is expected to take place in the southern Mediterranean countries (Fig. 3A), whose share will account for over 42% of the energy demand, compared to its current 28%. According to the projections for the year 2030, transport will continue to be the main consuming sector in the region and industry will account for the biggest increase in total final consumption, mostly because of its increase in the south. The Mediterranean's

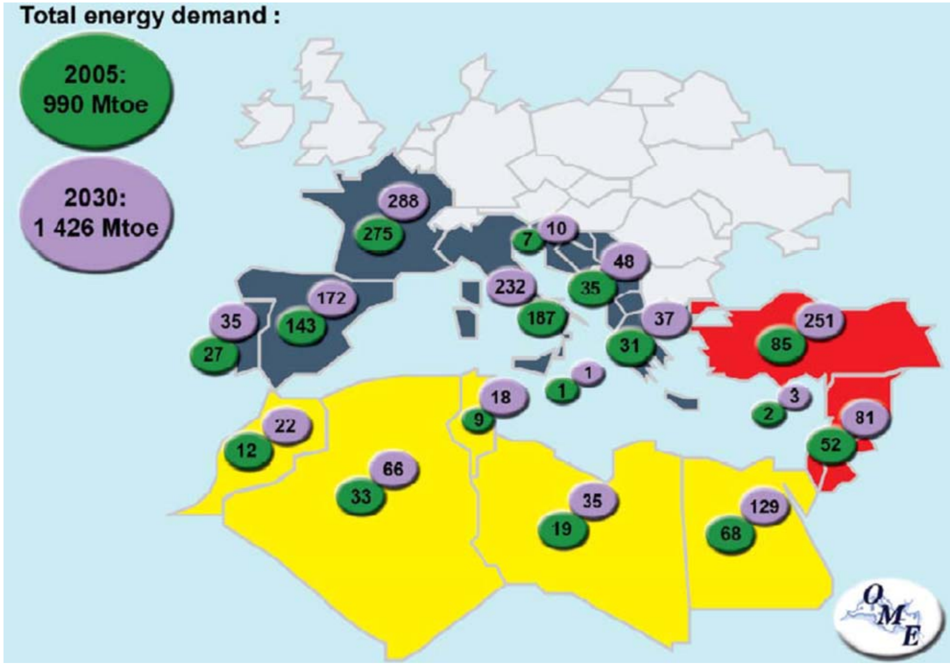

Fig. 2. Energy demand in different Mediterranean countries in 2005 and projected demand for 2030. These data were obtained from OME (2009) at: www.ome.org.

energy future will remain fossil fuel-based, fossil fuels accounting for about 80% of the total Mediterranean energy demand by 2030.

Oil will remain the dominant fuel in the Mediterranean energy mix (Fig. 3B), the demand for oil will continue to rise, along with that for transport fuels, especially diesel and gasoline. Eighty percent of the increase in the demand for oil will come from the southern Mediterranean, especially the southeast, whilst by 2030, the north will account for only 60% of total Mediterranean demand, as opposed to about 70% currently [7].

Oil production in the Mediterranean region is expected to increase by 20% by 2030, with an increase of about 40 Mtoe for refining capacity in the region by 2015, and a further 60 Mtoe by 2030. The increasing surplus of gasoline in the region will likely exceed the needs of its main importers, the USA and the EU, and it could potentially lead to a future predicament for the industry, the region and its populations [24].

The demand for gas in the Mediterranean is expected to rise from 244 Mtoe in 2005 to 432 Mtoe in 2030, and to account for 30%

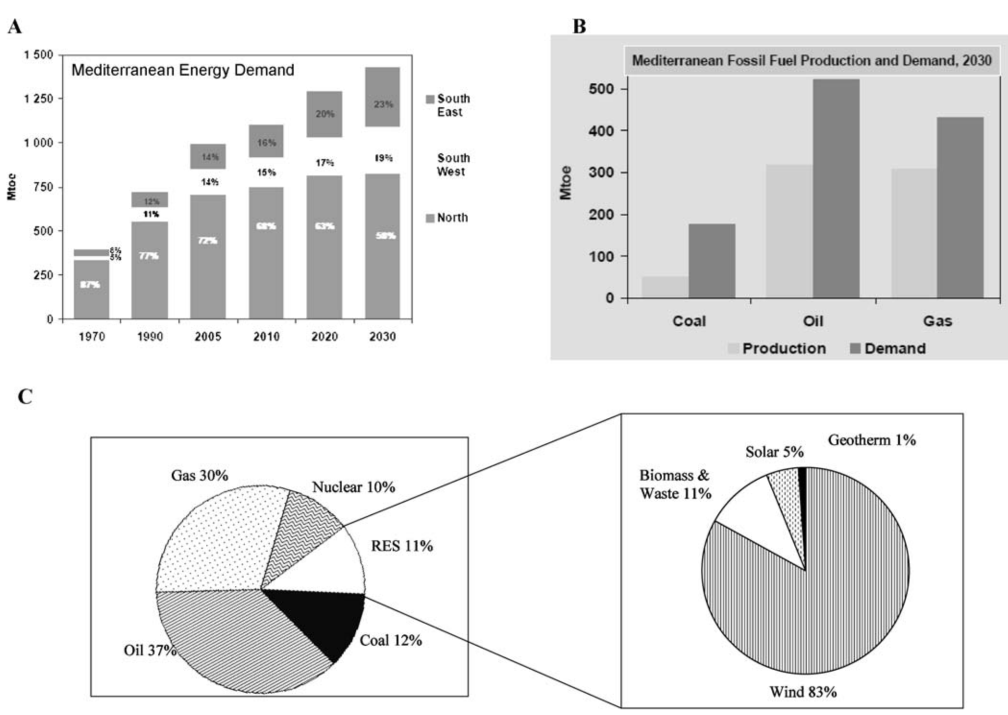

Fig. 3. (A) Energy demand by Mediterranean region. (B) Mediterranean fossil fuel production and demand. (C) Mediterranean renewable energy projection for 2030. RES: renewable energy sources. These data were obtained from OME (2009) at: www.ome.org.

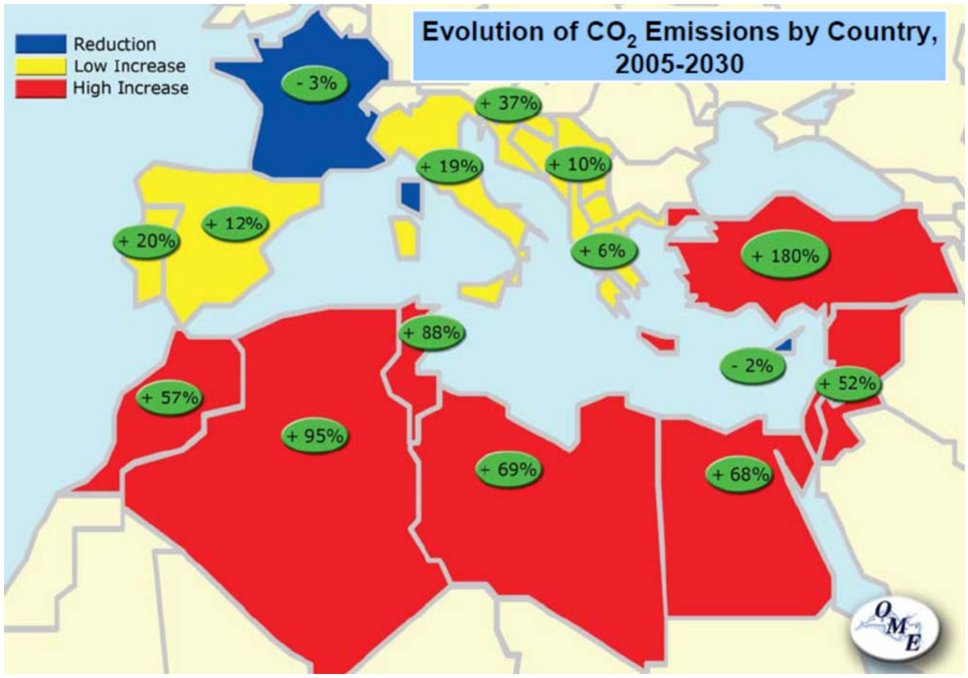

Fig. 4. Mediterranean CO_2 emissions for 2005 and projected for 2030. These data were obtained from OME (2009) at: www.ome.org.

of the total Mediterranean energy demand. The demand for coal will continue to grow strongly, at an average 1.7% per year, still accounting for 12% of the total energy mix in 2030.

Although renewable energy sources will be the fastest growing resources throughout the projection period, with an expected increase of more than 3.5% per year on average over the projected growth period, they will represent only 11% of the energy demand in 2030 (Fig. 3C).

Although the Mediterranean region is not one of the leading CO_2 emitters, it is particularly vulnerable to climate change. Diffenbaugh et al. [22] reported that elevated greenhouse gas (GHG) concentrations are dramatically increasing heat-stress risk in the Mediterranean, with the occurrence of hot extremes increasing by 200–500% throughout the region. Thus, huge mitigation efforts are needed in the region, where the Kyoto Protocol currently represents an under-exploited opportunity. According to the projected CO_2 emissions by the Mediterranean in the period 2005–2030 (Fig. 4), the northern Mediterranean countries are currently responsible for two-thirds of the CO_2 emissions, with Italy, France, and Spain as the main emitting countries. Over time, however, this situation is expected to change, with the northern and southern regions emitting equivalent shares of CO_2, because of new climate change legislation in the northern Mediterranean countries and economic development in the southern ones, coupled with significant fossil fuel exploitation. Among the southern Mediterranean countries, Turkey is by far the largest contributor to CO_2 emissions. Its emissions are expected to triple by 2030, such that they will account for 43% of all southern Mediterranean emissions. In 2030, CO_2 emissions in the southeastern Mediterranean countries will be almost twice those in the northern Mediterranean countries, and in the southwestern Mediterranean countries they will be three times higher.

In order to counteract the trend toward a fossil fuel-based economy in the Mediterranean, as an indispensable way of alleviating the climate change effects, tremendous efforts should be devoted to improving energy efficiency and diversifying the energy supply mix, including the large deployment of renewables. The use of renewable energy, especially biofuels, will give the Mediterranean a chance to provide a share of their energy from non-fossil energy sources, helping to mitigate the effects of climate change.

3. Bioethanol fuel production

As a sustainable alternative to a 100% oil-based economy, a new bio-economy can be developed based on biomass conversion into the liquid fuels that are well suited to transportation [25–28], which would considerably reduce the amount of CO_2 produced [29]. Bioethanol has been recognized as a potential alternative to petroleum-derived transportation fuels [30], with several known advantages, such as high octane number, low cetane number and high heat of vaporization [31].

In 2006, global production of bioethanol reached 13.5 billion gallons [32], accounting for more than 94% of global biofuel production [33]. Brazil and the US are the world leaders, together accounting for about 70% of the world bioethanol production. The potential demand for bioethanol as a fuel for transportation in EU countries, calculated on the basis of Directive 2003/30/EC [34], is estimated at 12.7 billion liters in 2010, in evident disproportion with the current EU production capacity of about 2 billion liters per year [35].

About 60% of the world's bioethanol is produced from sugar cane, 40% from other crops [36]. However, the use of sugar or starch as raw materials for fuel production competes with their use as food [37], and the supply is not expected to be sufficient to meet the increasing demand for ethanol fuel. To rise ethanol production levels, indirect land-use changes would be required, diverting land currently cropped for non-energy production to biofuel feedstock cultivation. However, possible GHG emissions from the induced land-use change could substantially alter the climate benefits of biofuel production and use [38–40].

Lignocellulosic biomass is an attractive alternative material for bioethanol fuel production. Lignocellulose is the most abundant renewable resource on Earth, and it constitutes a large component of the wastes originating from municipal, agricultural, forestry and some industrial sources. The more widespread geographical distribution of lignocellulose sources, compared to fossil reserves, can provide security of supply by using domestic sources of energy. The

use of lignocellulosic materials would minimize the potential conflict between land use for food (and feed) production and energy feedstock production. This raw material is less expensive than conventional agricultural feedstock and can be produced with lower input of fertilizers, pesticides, and energy. Biofuels from lignocellulose generate low net GHG emissions, reducing environmental impact, particularly on climate change.

Lignocellulosic biomass could produce up to 442 billion liters per year of bioethanol [41], with a total potential bioethanol production about 16 times higher than the current world bioethanol production [42].

Many reviews have been published on the main aspects of cellulosic ethanol processing and its progress [14,19,43–47]. Many lignocellulosic materials have been tested for bioethanol production [48], but the large-scale commercial production of bioethanol fuel from lignocellulosic materials has not been implemented yet. The main limiting factor is the higher degree of complexity inherent to the processing of this feedstock, related to the nature and composition of lignocellulosic biomass. Bioethanol production from lignocellulosic materials generally takes place in three phases: delignification of the lignocellulosic feedstock to liberate cellulose and hemicellulose from lignin; depolymerization of cellulose and hemicellulose, using acid or enzymatic hydrolysis, to produce free sugars; fermentation of mixed hexose and pentose sugars to produce ethanol. The cost of bioethanol production from lignocellulosic materials based on current technologies is relatively high: this is because the rate and yield of lignocellulose conversion to fermentable sugars is low, due to the resistant crystalline structure of cellulose and the physical barrier formed by the lignin surrounding the cellulose. Because the price of the feedstock represents a high share of the processing costs, the main challenge in developing an economical biomass-to-bioethanol process is to achieve rapid and efficient conversion of all of the sugars present in both its cellulose and hemicellulose fractions, thereby increasing the yield of the hydrolysis process [49–52].

One major problem is the availability of raw materials for ethanol production. Feedstock availability for bioethanol can vary considerably from season to season and it depends on geographic location. The price of the raw materials is also highly variable, which can strongly affect bioethanol production costs [53]. Currently, feedstock typically accounts for more than one-third of ethanol production costs [43]. Use of lignocellulosic residues, such as crop and wood residues and MSW, may result in a lower overall cost as compared to that of producing a ton of specially cultivated energy crops, where inputs must be invested to cultivate, fertilize and harvest them.

4. Feasibility of ethanol production from crop residues

Agricultural crop residues include field residues and processing residues. Field residues represent materials left in an agricultural field after the crop has been harvested, and they include stalks and stubble (stems), leaves, and seed pods. Processing residues, such as husks, seeds, bagasse, and roots, are those materials left after the processing of the crop into a usable resource. Harvesting of cereals, vegetables and fruits generates huge amounts of crop residues.

4.1. Ethanol production from crop residues

With respect to delignification of crop residues, analyses of the effects of substrate composition, cellulose crystallinity and particle size on the yields of enzymatic hydrolysis using bagasse and rice straw have shown that each type of lignocellulosic feedstock requires a specific pretreatment to optimize enzymatic hydrolysis [54]. Henderson et al. [55] reported an alkaline delignification procedure to separate cellulose, as the non-hydrolyzable product, from the lignin and hemicellulose, as the hydrolyzable product, of organic crop residues. The most efficient separations for the bagasse and corn stover were obtained by using two alkaline hydrolysis cycles with 0.5 N KOH at 70 °C.

Li and Champagne [56,57] reported relatively high fermentable glucose yields from depolymerization of crop residues through enzymatic hydrolysis. At 40 °C, with an enzyme loading of 800 units/g of delignified substrate, the percentages of conversion to glucose in 24 h were 65.4 and 51.1% on a delignified dry biomass basis for KOH-treated corn stover and bagasse, respectively. These studies showed that physical and/or chemical pretreatments (grinding, drying and phosphorylation) of non-hydrolyzable product have a great impact on the glucose yields from the saccharification process and that the optimal fiber pretreatment changes with the feedstock. The sequence of the pretreatments affected the enzymatic hydrolysis rate: crop residues ground before alkaline treatment and the use of a wet substrate yielded higher conversion rates. The hydrolysis rate was also found to increase when half of the enzyme dose was added at the beginning and half at the mid-point of the hydrolysis, rather than all at the beginning. Other studies involving bioethanol production from crop residues [42,54,58,59] reached similar conclusions.

Arvanitoyannis and Tserkezou [60] recently reviewed methods and current and potential uses of corn and rice wastes. Among these, the production of bioethanol from corn stover using simultaneous saccharification and fermentation (SSF) was reported as an economically advantageous and environmentally friendly process. SSF of high dry matter content resulted in a high ethanol concentration in the fermented slurry, thereby decreasing the energy demand in the subsequent distillation step [61]. An economic analysis of this ethanol production process indicated a cost saving of 6 cents per gallon, due to higher ethanol yields, lower operating costs and lower capital costs for the continuous process in a bubbling fluidized bed reactor with immobilized *Zymomonas mobilis* biocatalyst relative to a conventional batch process using yeast [62].

Based on current technologies, dried cellulosic biomass from crop residues has been shown to be readily converted to bioethanol at a rate of 300 l of ethanol produced per ton of oven-dried biomass [63].

4.2. Suitability of crop residues as raw materials for ethanol production

Energetic applications for crop residues may provide security of supply and mitigate climate change, and their use for ethanol production is strongly sustained in both the USA [64–66] and the EU [67,68]. In Canada, a much higher use of such residues to produce ethanol has been advocated by Champagne [63]. According to that author, one of the benefits of producing ethanol from crop residues is a reduction in the potential air, water and soil contamination associated with the land application of organic residuals. Champagne [63] estimated that if the total reported currently available residues (17.8 million tons biomass/yr) were converted to bioethanol, 5336 million liters of bioethanol could be produced from Canadian crop residues. However, the selection of crop residues as raw materials for ethanol production would have to be evaluated in light of their alternative possible applications, as underscored by Reijnders [69]. For an agricultural residue such as straw, for instance, one must first consider its application in building materials such as strawboard [70] and straw bales for load-bearing walls [68], while lower quality applications such as its use as a fuel might be more appropriate for wastes from a strawboard manufacturing facility or for building products after disposal. Among the possible alternative uses of crop residues, especially important is their use for stabilizing and increasing the

levels of soil organic carbon, with important effects on soil structure, limiting erosion, the provision of nutrients, counterbalancing acidification and water-holding capacity of soils and soil fertility [71–75]. Because of the negative effects of removing crop residues from the soil, Lal [76] suggested identifying alternate sources of biofuel feedstock, such as animal waste and MSW. On the other hand, Reijnders [69] proposed a reduction in residue removal from the field, with a higher fraction removed only for residues from annual crops generating relatively large amounts of biomass. As an alternative, selection of residues that contain relatively high levels of available cellulose and hemicellulose for removal and ethanol production has also been proposed. In the case of corn stover, this fraction consists of cobs, leaves and husks [77]. Another possible approach is returning the waste from processing crop residues – a residue rich in lignin and also containing un-reacted cellulose and hemicellulose [47] – to the field.

5. Potential of bioethanol production from crop residues in the Mediterranean

There is a large, unutilized energy potential in the agricultural waste fraction of the Mediterranean region, where 29% of the total land area is devoted to agricultural production (FAOSTAT). To evaluate the potential of bioethanol production from agricultural residues discharged by Mediterranean countries, data of biomass – crop, fruit and vegetable – production were obtained from FAOSTAT for the following countries: Albania, Algeria, Andorra, Bosnia and Herzegovina, Croatia, Cyprus, Egypt, France, Greece, Israel, Italy, Jordan, Lebanon, Libyan Arab Jamahiriya, Malta, Montenegro, Morocco, Portugal, Slovenia, Spain, Syrian Arab Republic, Tunisia and Turkey. Data on the potential distribution of bioenergy crops were obtained from Tucka et al. [78].

5.1. Mediterranean agricultural production

The cereals barley, wheat, oat and rye can now be potentially grown throughout the northern part of the Mediterranean, excluding countries located south of latitude 441N. Oats have a lower maximum summer temperature requirement than the other cereals [79]. Barley is most widespread, due to its lower water requirement [79] and greater resistance to high temperatures [80]. However, temperatures above 30 °C may adversely affect the grain fill of all cereals [81]. Sorghum is more widespread in the south, and today, it can potentially be grown in up to 25% of southern Europe, although it is a native of the tropics.

In 2007, the Mediterranean countries produced 85 million tons of wheat, 43 million tons of maize, 34 million tons of barley, 10 million tons of rice, 2.7 million tons of oats, 1.4 million tons of sorghum, 0.76 million tons of rye, and 24,802 tons of millet. Wheat is mostly produced by Algeria (26 million tons), France (33 million tons) and Turkey (18 million tons), with a significant contribution from Italy (7.3 million tons), Egypt (7.4 million tons), Spain (6.4 million tons) and the Syrian Arab Republic (4.5 million tons) as well. France (13 million tons), Italy (10 million tons) and Egypt (7 million tons) are the main contributors to maize production, followed by Turkey (3.9 million tons), Spain (3.6 million tons), Greece (1.8 million tons) and Croatia (1.4 million tons). Spain (11.7 million tons), France (9.5 million tons) and Turkey (7.4 million tons) are the most important producers of barley, followed by Italy (1.2 million tons), Libyan Arab Jamahiriya (1 million tons) and Albania (1.4 million tons). Egypt contributes 66% of rice production (10 million tons), with Italy (1.5 million tons), Spain (0.7 million tons) and Turkey (0.68 million tons) contributing most of the rest. Spain accounts for almost 50% of oat production, with the main contributions for the other 50% provided by Italy (0.40 million tons), France (0.44 million tons) and Turkey (0.2 million tons). Egypt produces 57% of sorghum, and France (0.3 million tons) and Italy (0.2 million tons) account for most of the rest. Turkey (0.26 million tons), France (0.12 million tons) and Spain (0.26 million tons) are the main contributors to rye production.

The starch crops potato and sugar beet have a wide potential distribution throughout the Mediterranean, while they do not currently grow north of latitude 651N. Sugar cane, usually grown in tropical and subtropical areas, could potentially be grown in very small areas in southwestern Europe under the current climate, where high temperatures combine with high rainfall.

In 2007, the overall production of sugar beet, potato and sugar cane was 70, 26 and 17 million tons, respectively. Sugar beet production is mainly supplied by France (32 million tons) and Turkey (15 million tons), and in minor amounts by Egypt (5.6 million tons), Italy (4.6 million tons), Morocco (3 million tons) and Spain (5.1 million tons). Spain (2 million tons), France (6 million tons) and Turkey (4 million tons) represent the main producers of potato, followed by Egypt (2.6 million tons), Algeria (1.9 million tons), Italy (1.8 million tons) and Morocco (1.4 million tons).

Egypt contributes 95% of the Mediterranean's sugar cane production, the remainder coming mainly from Morocco (0.9 million tons) and Spain (0.06 million tons), with a small amount (5100 tons) from Portugal.

Due to their climatic requirements, oilseed rape and linseed have the current potential to be grown across most of the Mediterranean region. Field mustard and hemp are much less widely distributed, due to lower maximum temperature and higher minimum rainfall requirements. Sunflower, castor and olive currently have a wide potential distribution at latitudes south of 541N. Groundnut and sunflower are restricted to small areas in southwestern Europe, due to a high minimum temperature requirement.

In 2007, 16 million tons of olives were produced in the Mediterranean area with the main contributions from Spain (5.8 million tons), Italy (3.5 million tons), Greece (2.6 million tons) and Turkey (1.5 million tons), followed by Tunisia (0.9 million tons), Morocco (0.7 million tons), Egypt (0.32 million tons) and Algeria (0.3 million tons). France was responsible for 96% (4.7 million tons) of rapeseed production in 2007. France (1.4 million tons), Turkey (1 million tons), Spain (0.74 million tons) and Italy (0.27 million tons) were the main contributors to the 3.6 million tons of sunflower seeds produced in 2007. On the other hand, only low amounts of groundnut (198,000 tons), linseed (55,000 tons), hempseed (5588 tons) and castor oil seed (100 tons) were produced.

Mediterranean countries produced 69 million tons of fruits in 2007. As shown in Fig. 5A, grapes were the most abundantly produced fruit (39%) in the Mediterranean region, followed by oranges (15%), apples (12%), tangerines/mandarins/clementines (7%), peaches/nectarines (7%), lemons (4%) and pears (3%). The main Mediterranean producers of fruit were Spain (23%), Italy (19%), Turkey (15%), France (12%) and Egypt (10%) (Fig. 5B). The main contribution to grape production was provided by Italy (28%), followed by France (22%), Spain (20%) and Turkey (13%) (Fig. 5C).

A total of 99 million tons of vegetables were produced in the Mediterranean region in 2007, with tomatoes accounting for 43% of total vegetable production (Fig. 6A). Turkey, Egypt, Italy and Spain were the main producers of vegetables, providing 25, 16, 14 and 13% of total production, respectively (Fig. 6B), and 28, 21, 17 and 10% of tomato production (Fig. 6C), respectively.

5.2. Estimation of potential ethanol production from crop residues in the Mediterranean

The potential for ethanol production from cereal residues was estimated for the main producing Mediterranean countries. As reported above, very large amounts of cereals are produced in

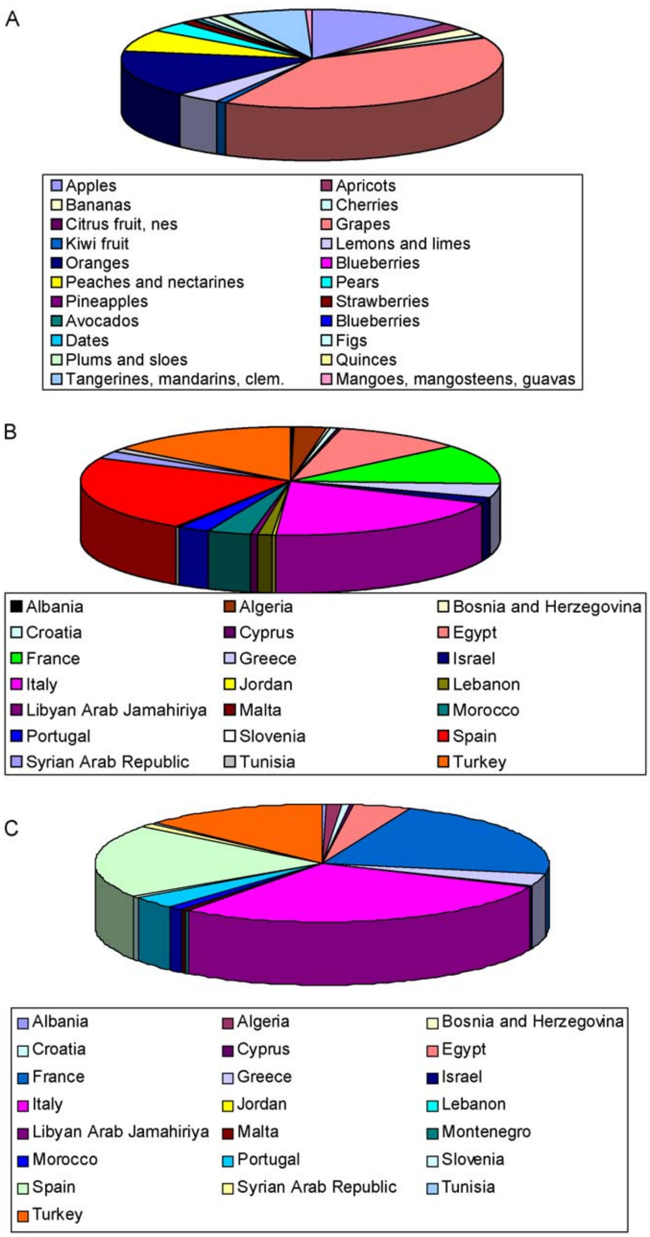

Fig. 5. (A) Abundance of the different fruits grown in the Mediterranean. (B) Distribution of total fruit production among different countries. (C) Distribution of grape production among different countries.

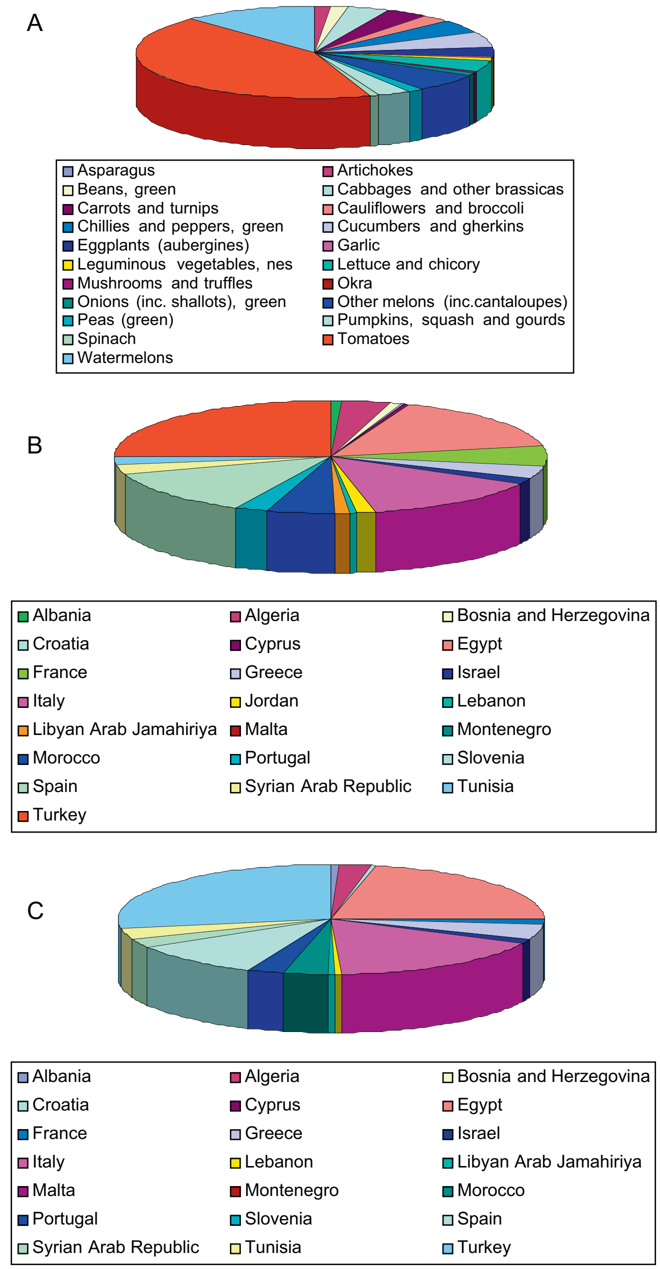

Fig. 6. (A) Abundance of the different vegetables grown in the Mediterranean. (B) Distribution of total vegetable production among different countries. (C) Distribution of tomato production among different countries.

the Mediterranean region, with wheat, maize and barley representing the most abundantly cultivated cereals, accounting for 48, 24 and 19% of cereal crop production, respectively. The corresponding crop residues, wheat straw, corn stover and barley straw, can produce high yields of ethanol, as they contain 38, 38 and 42% cellulose, respectively [82]. Moreover, cereals generate large amounts of residue. The straw-to-grain ratio is usually 1:1 for corn, soybean and oats, and 1.5:1 for wheat, barley, rice, rye, sorghum and millet [83]. However, an estimation of the amounts of cereal (field) residues corresponding to 50% production would tend to overestimate actual biomass and carbon availabilities because, as already mentioned, a fraction of the residues must remain in the field to ensure soil fertility. In addition, traditional uses for agricultural residues such as straw and stover, including animal bedding and mulching, further reduce the current biomass availability. Therefore, the cereal residues available for energy generation are estimated to amount to only about 15% of total agricultural production [14]. The potential ethanol production capacity from this residual biomass was estimated for the main Mediterranean countries producing cereals (Table 1), considering a rate of 300 l of ethanol produced per ton of biomass [63]. This estimation showed that high volumes of ethanol could be produced from cereal residues in France (2.6 Gl), Turkey (1.4 Gl), Spain (1.1 Gl), Egypt (0.99 Gl) and Italy (0.9 Gl).

On the other hand, starch residues were not considered as potential raw materials for efficient large-scale ethanol production in the Mediterranean, because of the lesser extent of lands devoted to their cultivation in the region. Moreover, less residues are left in the field during the harvesting of starch crops, corresponding to 25% of total crop production [83]. Besides, the cellulose content of starch crop residues is lower than that of cereal crop residues, the cellulose fraction representing only 20% [84] and 28% [85] of sugar beet and potato residues, respectively.

Table 1
Amounts of residues from cereal crops, olive harvesting, and tomato and grape processing in the Mediterranean producer countries, and estimation of potential ethanol production capacity from cereal crop residues and olive tree pruning residues (hypothesising a yield of 300 l per ton), and from tomato and grape waste (hypothesising a yield 150 l per ton).

Country	Crop	Crop production 2007 (Mt)	Crop residue (Mt)	Ethanol		
				Ml	Mton	Mtoe
France	Cereal	58.7	8.8	2641	2.1	3.2
Turkey		30.2	4.5	1359	1.0	1.6
Spain		24.1	3.6	1086	0.86	1.34
Egypt		22.0	3.3	993	0.79	1.23
Italy		20.5	3.0	922	0.73	1.14
Spain	Olives	5.79	1.74	522	0.416	0.65
Italy		3.48	1.04	312	0.248	0.39
Greece		2.60	0.78	234	0.186	0.29
Turkey		1.52	0.46	138	0.110	0.17
Italy	Grapes	8.5	1.70	255	0.203	0.36
France		6.5	1.30	195	0.155	0.24
Spain		6.0	1.20	180	0.143	0.22
Turkey		3.9	0.78	167	0.133	0.28
Turkey	Tomato	9.9	2.97	445	0.354	0.55
Egypt		7.5	2.26	339	0.270	0.42
Italy		6.0	1.81	270	0.215	0.34
Spain		3.6	1.08	162	0.129	0.20
Total ethanol production				10,220	8.042	12.62

Additional agricultural products yielding high amounts of residue that could represent potential raw materials for ethanol production in the Mediterranean include olive, tomato and grape (Table 1). For the latter two crops, wastes issued from their processing were assessed as possible raw materials for ethanol production, since processing absorbs most of cultivation products for these species.

A typical olive tree pruning lot includes 30% wood that is separated and put to domestic use as firewood, with no other industrial applications [86], thus generating a large fraction of residual biomass available for energy production (Table 1) in several Mediterranean countries. Olive tree pruning residue has a good potential capacity for ethanol production, as olive wood has a cellulose content of 34% [87]. Most of the tomatoes cultivated in the Mediterranean (around 80%) are processed into ketchup, pasta sauce and canned goods, generating processing residue that consists mainly of skin and seeds (tomato pomace) and that can represent up to 40% of the raw material [88]. During wine production, grape waste corresponding to 20% of the processed grape is typically produced [89]. A cellulose content of around 20% has been reported for both tomato [90] and grape processing residues [91]. Taking into account these data, huge amounts of tomato and grape pomace are generated in some Mediterranean countries (Table 1). The potential ethanol production capacity from olive tree pruning residues was estimated, hypothesizing the same ethanol production rate as that from cereal residues (Table 1). Taking into account the lower cellulose content of tomato and grape pomace, the potential ethanol production capacity from these residues was evaluated assuming a rate equal to half of that from cereal residues (Table 1).

6. Feasibility of ethanol production from MSW

The cellulose content in MSW is mainly from paper wastes. The MSW fractions of office paper, coated paper, newsprint and corrugated boxes contain 87, 42, 48 and 57% cellulose, respectively [92]. Food waste contains a variable amount of cellulose, accounting for around 50% of the residue on average [92].

6.1. Development of a process for bioethanol production from MSW

Only scarce information is available regarding the use of MSW as a biomass for bioethanol production. Yáñez et al. [93] reported a dilute acid pretreatment (180 min with 3%, w/w of H_2SO_4) of residual corrugated cardboard, rendering the pretreated waste susceptible to enzymatic hydrolysis into hemicellulosic sugars and glucose by commercial enzymes of "Celluclast" cellulases (28 FPU/g of substrate) from *Trichoderma reesei* and "Novozym" β-glucosidase (360 IU/g of substrate) from *Aspergillus niger* provided by Novo Nordisk Bioindustrial.

Mtui and Nakamura [94] applied a pre-hydrolysis stage (carried out with dilute strong acid followed by steam treatment at 120 °C for 15 min) and enzymatic hydrolysis (with cellulase enzyme extracted from *T. reesei*, incubated at 55 °C for 6 h) to lignocellulosic solid wastes from selected sites in Tanzania. They achieved a glucose concentration of 0.13 and 0.05 g/l (corresponding to 1 g of pretreated lignocellulosic material) from solid waste samples with high lignocellulose content (93%) and low lignocellulose content (14%), respectively.

Li et al. [95] compared 15 different pretreatments of selected biodegradable MSW fractions (carrot peelings (CP) and potato peelings (PP) typical of kitchen waste, grass (G) typical of garden waste and newspaper (NP) and scrap paper (SP) typical of paper/card fractions) to obtain the highest glucose yield for bioethanol production. Pre-hydrolysis treatments consisted of dilute acid (H_2SO_4, HNO_3 or HCl, 1 and 4%, 180 min, 60 °C), steam treatment (121 and 134 °C, 15 min), microwave treatment (700 W, 2 min) or a combination of two of these. Enzymatic hydrolysis was carried out with cellulases from *T. reesei* and *T. viride* (10 and 60 FPU/g of substrate) (Sigma). The highest glucose yield (73%) was obtained with a pre-hydrolysis treatment of 1% H_2SO_4 followed by steam treatment at 121 °C, and enzymatic hydrolysis with *T. viride* at 60 FPU/g substrate. The contributions of enzyme loading and acid concentration were significantly higher (49.39 and 47.70%, respectively) than the contribution of temperature during the steam treatment (0.13%) to the glucose yield.

Comparing hydrolysis of primary municipal wastewater sludge, secondary municipal wastewater sludge and municipal biosolids,

Li and Champagne [56,57] found the highest fermentable glucose yield from the primary municipal wastewater sludge. Both wet and dry substrates were subjected to different combinations of pretreatments, including drying, grinding, KOH, HCl, and HCl followed by KOH alkaline delignification at 40 °C for a period of 24 h. Results indicated that the cellulose in primary sludge is readily accessible to the enzymes. The KOH pretreatment was not particularly effective on the primary sludge, increasing its digestibility by only 4%. Similarly, when the primary sludge was treated with HCl, the glucose yield increased by 11.5% over that observed without acid and alkaline treatment (31.1%). The results implied that conversion of the cellulose contained in primary sludge into bioethanol might present a valuable waste-management alternative when employed as a wet feedstock, as drying and grinding are not necessary.

6.2. Suitability of MSW as raw material for ethanol production

MSW may be considered an alternative sustainable source of bioethanol and biogas [95–97]. Ethanol production from MSW has environmental and economic benefits. However, when compared with the use of MSW for biogas production, ethanol production may be less advantageous.

In a recent study, Murphy and Power [98] analyzed four scenarios for energy generation from newspaper: lignocellulosic biomass conversion to ethanol (transport fuel); co-digestion with the organic fraction of MSW and production of CH_4-enriched biogas (transport fuel); co-firing with the MSW residue in an incinerator; gasification of newspaper as a sole fuel. Comparison of the profit/gate fee per ton of newspaper showed that the biogas scenario has a large economic advantage over the others, and the GHG analysis indicated that the biogas scenario generates the best net GHG savings.

Kalogo et al. [99] modeled a facility for conversion of MSW into ethanol that employs dilute acid hydrolysis and gravity pressure vessel technology, estimating its life-cycle energy use and air emissions. Results were compared with life-cycle assessments (LCAs) of vehicles fuelled with gasoline, corn–ethanol, and energy crop cellulosic ethanol, assuming the ethanol is utilized as E85 (blended with 15% gasoline) in a light-duty vehicle. MSW–ethanol production was also compared, as a waste-management alternative, with landfilling with gas-recovery options. For MSW-derived ethanol, the total energy use per vehicle mile traveled proved to be less than that of corn–ethanol and cellulosic ethanol. Energy use from petroleum sources for MSW–ethanol was lower than for the other fuels. MSW–ethanol used in vehicles reduced net GHG emissions by 65% compared to gasoline, and by 58% compared to corn–ethanol. Relative GHG performance with respect to cellulosic ethanol depended on whether MSW classification was included or not. Thus, converting MSW into ethanol would result in a net fossil energy savings of 397–1830 MJ/million tons MSW compared to a net fossil energy consumption of 177–577 MJ/million tons MSW for landfilling. However, landfilling with gas recovery, either for flaring or for electricity production, would result in greater reductions in GHG emissions than the MSW-to-ethanol conversion.

Stichnothe and Azapagic [100] carried out a LCA to estimate the GHG emissions from bioethanol production using two alternative feedstocks, both derived from household waste: refuse-derived fuel (RDF) and biodegradable municipal waste (BMW). An integrated waste-management system was considered, taking into account recycling of materials and production of bioethanol in a combined gasification/biocatalytic process. For the functional unit defined as the 'total amount of waste treated in the integrated waste-management system', the best option was to produce bioethanol from RDF—this saved up to 196 kg CO_2 equiv. per ton of MSW, compared to the current waste-management practice in the UK. However, if the functional unit was defined as 'MJ of fuel equiv.' and bioethanol was compared with petrol on an equivalent energy basis, the results showed that bioethanol from RDF offered no saving of GHG emissions compared to petrol, whereas bioethanol from BMW offered significant GHG savings potential over petrol. For a biogenic carbon content of 95%, the life-cycle GHG emissions from bioethanol were 6.1 g CO_2 equiv./MJ, which represents a savings of 92.5% compared to petrol. If the biogenic carbon of the BMW feedstock exceeded 97%, the bioethanol system became a carbon sequester. For instance, if waste paper with a biogenic carbon content of almost 100% and a calorific value of 18 MJ/kg was converted into bioethanol, a savings of 107% compared to petrol could be achieved. Compared to paper recycling, converting waste paper into bioethanol would save 460 kg CO_2 equiv./ton waste paper, or eight times more than recycling.

Chester and Martin [101] examined the major processes required to support a lignocellulosic MSW-to-ethanol infrastructure, computing cost, energy, and GHG effects for California. Their analysis was performed on MSW destined for landfills, for an ethanol plant employing a pretreatment by cocurrent dilute acid pre-hydrolysis, before enzymatic hydrolysis. Reductions in fossil energy consumption resulted primarily from displacement of gasoline and avoided emissions at the landfill (140 PJ/yr). This was only partially offset by fossil energy increases in the plant and classification phases (32 PJ/yr), with a resulting fossil energy reduction of 110 PJ/yr. On the other hand, the authors found that ethanol production from MSW cannot be unequivocally justified from the perspective of net GHG avoidance. The avoided impact of diverting organic waste from the landfill presents the greatest system uncertainty. The net GHG impact is ultimately dependent on how well landfills control their emissions of decomposing organics. There is currently considerable uncertainty surrounding the recovery efficiency of landfill emission controls. A better understanding of carbon sequestration and methane capture performance within landfills is necessary before stronger conclusions can be drawn.

7. Potential ethanol production from MSW in the Mediterranean

Unprocessed MSW in the Mediterranean region consists primarily of paper/cardboard, kitchen waste, garden waste, textiles, fines and miscellaneous (combustibles and others).

In France, Greece, Italy, Portugal, Spain, Cyprus, Malta, Slovenia, Croatia and Turkey, an average 538 kg of MSW per capita was produced in 2007, corresponding to a total amount of 135 million tons [102]. Organic and paper fractions represented the main MSW fractions, accounting for 40 and 20%, respectively [103].

In Mashreq and Maghreb countries (Algeria, Egypt, Jordan, Lebanon, Morocco, Syria, Palestinian Authority and Tunisia), 254 kg of MSW were produced per capita in 2002, with a total amount of 42 million tons [104], the organic fraction representing 55–70% of total weight. According to a study by the Solid Waste Division of the Israeli Ministry of Environmental Protection, in 2006, each person in Israel generated 560 kg of MSW, with a total quantity of waste of around 6 million tons, including municipal and industrial waste [105].

The most common method of MSW management in the Mediterranean is dump disposal which absorbs on average 40–60% of the produced MSW, reaching 90% or even more in some countries, such as Algeria, Morocco and Egypt. On the other hand, recycling, where available, absorbs a very low fraction (5–20%) of the total MSW. The collection, treatment and/or disposal of MSW is a major problem throughout the Mediterranean region – from a total absence of waste-collection systems to dysfunctional ones, from non-existent recycling schemes to heaps of recyclable materials lying unprocessed at waste-processing plants,

from uncontrolled dump sites to rejection of modern sanitary landfills or waste – treatment facilities by local communities, and the list goes on.

With the advances in cellulosic ethanol technologies, the Mediterranean could use the cellulosic content of MSW as a transportation fuel feedstock and simultaneously reduce externalities associated with waste disposal. Assuming between 60 and 90% practical yields for ethanol production, the Mediterranean could produce between 17 and 25 billion liters per year of ethanol from 50% of the 180 million tons of waste currently produced annually.

8. Case study: development of an ethanol-production process from olive wastes

Harvesting and processing of olives in the Mediterranean produce huge amounts of lignocellulosic residues (olive tree pruning residues and olive cake) which are not currently being exploited. More than 8×10^6 ha of olive trees are cultivated worldwide, most of them in Mediterranean countries, where olive tree pruning produces a largely available residue. Olive tree wood has limited application as firewood in domestic uses, but the rest of the pruning residue (together with wood when it is not separated) is usually burned in the fields to prevent propagation of olive tree diseases.

Olive oil production represents one of the most important economic agro-food sectors in the Mediterranean Basin. Southern Europe (Spain, Italy and Greece) is the world's largest producer of olive oil, accounting for 79% of world olive oil production in 2005, when they produced around 2 million tons of olive oil [106]. Moreover, the global demand for olive oil is growing due to its health-promoting effects. The traditional oil industry generates two downstream byproducts, olive cake (residue) and olive mill wastewater, which can cause serious problems of environmental pollution. Crude olive cake, the leftover solids following the pressing of olives, is made up of pressed olives, including stones, constituting a mixture of skin, pulp and seeds. It comprises approximately 35% of the olive's starting weight and is available in appreciable quantities in the Mediterranean area. Global annual production of olive cake has been estimated to approach 4×10^8 kg [107]. Olive cake is 95% (w/w) dry and essentially consists of strongly lignified cell walls (28.1%), is rich in cellulose (15.9%) and xylan (20.9%) on a dry weight basis, and contains a small amount of arabinan (1.9%).

Today, the three-phase centrifugation process for extracting olive oil is being replaced by a new and more environmentally friendly technology (two-stage extraction). This technology significantly reduces the amount of wastewater produced, but generates a new type of waste, a solid residue called olive pulp (OP). It is estimated that 800 kg of OP is produced per ton of olives processed [108], resulting in approximately 8 million tons of OP generated per year in Southern Europe [106]. At present, OP is either discarded to the environment or combusted with low calorific value.

Use of all of the residues generated from both harvesting and processing of olives in the Mediterranean – olive tree pruning, olive cake and OP – as raw materials for ethanol production is described.

8.1. Ethanol from olive tree pruning residue

The olive tree residues obtained from pruning were just recently tested as a raw material for ethanol fuel production. Enzymatic hydrolysis of olive tree biomass was then investigated for the first time [86,109], by analyzing the influence of steam-explosion pretreatment on sugar recovery in both solids and liquids and the enzymatic hydrolysis of solids. Cara et al. [86] assessed digestibility of olive tree wood after a steam-explosion pretreatment (at 190, 210, 230 and 240 °C for 5 min) with or without a further delignification step by alkaline peroxide treatment. Enzymatic hydrolysis was performed using a commercial cellulolytic complex supplemented with β-glucosidase at 10% (w/v) pretreated material concentration. Delignification did enhance enzymatic hydrolysis yields of steam-pretreated olive tree wood. Up to 80% of the lignin in the original wood was solubilized, leaving a cellulose-rich residue that led to a concentrated glucose solution (51.3 g/l after 72 h enzymatic hydrolysis in the best case). As a maximum overall process yield, 28.8 g of sugars were recovered of 54.7 g available (52.6%) from 100 g of raw material, at the lowest steam pretreatment temperature assayed.

Influence of solid loading (in the range of 2–30%, w/v) on enzymatic hydrolysis of steam-exploded or liquid hot water-pretreated olive tree biomass with and without an alkaline delignification step was also analyzed [109]. Enzymatic hydrolysis at high substrate concentrations (≥20%) was possible, yielding a concentrated glucose solution (>50 g/l). Nevertheless, a cellulose fraction of the pretreated residue remained unaltered.

The feasibility of ethanol production by simultaneous SSF of steam-exploded olive tree wood was demonstrated by Ruiz et al. [87]. Steam explosion at different temperatures was applied, and the water-insoluble fraction of the steam-pretreated delignified olive tree wood was used as a substrate at 10% (w/v) concentration for an SSF process by a cellulolytic commercial complex and *Saccharomyces cerevisiae*. After 72 h fermentation, ethanol concentrations up to 30 g/l were obtained in delignified steam-pretreated olive tree wood at 230 °C for 5 min. After this pretreatment of the solid residue and the SSF process, 7.5 g of ethanol was obtained from 100 g of olive tree wood, corresponding to 43% of theoretical. Relative to the raw material, 95.1 l ethanol/ton olive tree wood may be obtained.

Different pretreatment conditions were evaluated for olive tree biomass in a SSF process with a cellulolytic commercial complex and *S. cerevisiae* [110,111]. Cara et al. [110] investigated the production of ethanol fuel after steam pretreatment of olive tree pruning residues with and without water or sulfuric acid impregnation. The influence of both pretreatment temperature (in the range 190–240 °C) and impregnation conditions (with water or sulfuric acid solution) on sugar and ethanol yields was assessed by enzymatic hydrolysis and SSF of pretreated solids. The maximum ethanol yield (7.2 g ethanol/100 g raw material) was obtained from water-impregnated, steam-pretreated residue at 240 °C. Nevertheless, if hemicellulosic sugars solubilized to liquids during the pretreatment are taken into account, up to 15.9 g ethanol/100 g raw material may be obtained after pretreatment at 230 °C and impregnation with 1% (w/w) sulfuric acid, assuming theoretical conversion of these sugars to ethanol.

The production of fermentable sugars from olive tree biomass was analyzed by Cara et al. [111] by dilute acid pretreatment and further saccharification of the pretreated solid residues, under different pretreatment conditions (0.2%, 0.6%, 1.0% and 1.4% (w/w) sulfuric acid concentrations with temperatures in the range of 170–210 °C). Attention was paid to sugar recovery in both the liquid fraction issued from the pretreatment (pre-hydrolysate) and the water-insoluble solid. As a maximum, 83% of the hemicellulosic sugars in the raw material were recovered in the pre-hydrolysate obtained at 170 °C, 1% sulfuric acid, but the enzyme accessibility of the corresponding pretreated solid was not very high. The maximum enzymatic hydrolysis yield (75%) was attained from a pretreated solid (at 210 °C, 1.4% acid concentration) in which cellulose solubilization was detected. Taking into account fermentable sugars generated by the pretreatment and the glucose released by enzymatic hydrolysis, a maximum overall sugar yield (36.3 g sugar/100 g raw material) was obtained by pretreating the olive tree biomass at 180 °C with 1% sulfuric acid for 10 min, representing 75% of all sugars in the raw material. The hydrolysate obtained

from this raw material was a mixture of hexoses and pentoses (with glucose and xylose, respectively, as the main sugars).

The fermentation of olive tree biomass hydrolysates, obtained by sulfuric and phosphoric acid pre-treatment under atmospheric pressure (90 °C), has been reported with *Pachysolen tannophilus* as the fermenting microorganism [112–113]. Romero et al. [112] reported on *P. tannophilus* fermentation of hydrolysates obtained from olive tree pruning residues pretreated with different sulfuric acid concentrations (0.5–4 N) at 90 °C for 240 min. The ethanol yields were much higher than xylitol yields under all conditions tested. The maximum ethanol yield (0.38 g/g) was reached with the hydrolysate obtained with 0.75 N sulfuric acid. Under these conditions, conversion of the hemicellulose fraction was 92%. Higher acid concentrations allow total hydrolysis of the hemicellulose, but the ethanol yields resulting from the fermentation were lower, such that the increase in operational costs were probably no longer justified.

Romero et al. [113] tested the feasibility of *P. tannophilus* fermentation following hydrolysis with (0.3–8 N) phosphoric acid to hydrolyze the hemicellulosic fraction of milled olive tree pruning residues at 90 °C for 240 min. The maximum ethanol yield (0.38 kg/kg, equivalent to 74.5% of the theoretical yield) was obtained when hydrolyzing with 0.5 N phosphoric acid, but hemicellulose conversion was incomplete under these operational conditions. Higher acid concentrations led to higher hydrolysis of hemicellulose, but the ethanol yields resulting from the fermentation were lower. Moreover, the cellulose fraction remained unaltered. Product yields might be significantly improved by taking into account conversion of cellulose-derived glucose.

Diaz et al. [114] showed that *Pichia stipitis* -reported as the most promising naturally occurring C5-fermenting microorganism- can be used for the effective fermentation of sugars contained in the hydrolysates from dilute (1% w/w) sulfuric acid pretreatment at 190 °C for 10 min of olive tree biomass, after a detoxification treatment to reduce the inhibitory effects [115] of compounds such as acetic acid, formic acid, and furfural found in these hydrolysates [111]. Effective fermentation required dilution of the hydrolysate and either over-liming or activated charcoal treatment. Ethanol yields obtained from detoxified hydrolysates, varying from 0.35 to 0.42 g ethanol/g sugar, were in the range of reported values for other lignocellulose substrates.

8.2. Ethanol from olive cake

El Asli and Qatibi [107] demonstrated that olive cake may be a suitable feedstock for ethanol production and selected the optimal H_2SO_4 concentrations and temperatures for pretreatment. The amount of acid added was increased up to 4% (w/v), beyond that typically used for dilute acid pretreatment of corn stover, because at lower acid loadings the pH of the olive cake hydrolysate was higher than desirable to achieve optimal pretreatment. Increasing the acid concentration resulted in a lower final pH and an increased release of pentoses from the olive cake, but some sugar degradation occurred, as evidenced by the increased concentration of 5-hydroxymethylfurfural and furfural in the hydrolysates. Pretreatments were performed at 160, 170 and 180 °C with 10 and 20% (w/v) loading of solids. Pretreatment of olive cake at 10% (w/v) loading resulted in the release of more sugars than at 20% loading, indicating limitations of these pretreatment conditions for solubilizing hemicellulose at higher loadings of solids. Hydrolysis with 1.75% (w/v) sulfuric acid and heating at 160 °C for 10 min, followed by chemical elimination of fermentation inhibitors by over-liming, generated a hydrolysate supernatant that was efficiently fermented by *Escherichia coli* FBR5. All of the glucose was consumed during the fermentation of the 160 °C hydrolysates within 20 h, while conversion of the pentose sugars xylose and arabinose required an extra day. Increasing the pretreatment temperature to 180 °C resulted in lower concentrations of soluble sugars, likely due to their degradation, and in failed fermentations, presumably due to the inhibitory effect of the much higher concentrations of furfural and 5-hydroxymethylfurfural. The ethanol yield was 0.45 g per 1.0 g of sugar present at the start of fermentation and 0.47 g per 1.0 g of sugar consumed, in comparison with a theoretical yield of 0.51 g ethanol/g glucose or xylose; 8.1 g of ethanol/l was obtained from hydrolysates containing 18.1 g of soluble sugars.

A process of ethanol production from OP – the waste generated from the two-step centrifugation process of olives – has been reported by Georgieva and Birgitte [116]. Enzymatic hydrolysis and subsequent glucose fermentation by baker's yeast were evaluated for OP with 10–30% dry matter. Enzymatic hydrolysis resulted in a 75% increase in glucose concentration, giving final glucose yields near 70%. Fermentation of undiluted OP hydrolysate resulted in the maximum ethanol produced (11.2 g/l) with a productivity of 2.1 g/l h. Ethanol yields were similar for all tested OP hydrolysate concentrations and were in the range of 0.49–0.51 g/g. Results showed that yeast could effectively ferment OP hydrolysate, even without nutrient addition, revealing the tolerance of yeast to OP toxicity. Because of its low xylan (12.4%) and glucan (16%) contents, this specific type of OP is not suitable for producing only ethanol and thus, bioethanol production should be integrated with the production of other value-added products.

9. The main constraints on ethanol production in the Mediterranean region and the future challenges

An uneven geographical distribution of agricultural biomass resources is seen among the Mediterranean countries. Whereas on the one hand there is great potential for bioethanol production from agricultural residues in some countries (France, Turkey, Spain, Egypt and Italy), on the other, lack of sufficient amounts of agricultural biomass for effective ethanol production is observed for the entire eastern Asian side and for most of the Maghreb region, where the prevalence of desert lands prevents the culturing of most agricultural products. As an alternative to the agricultural residues, MSW could provide a medium- to long-term solution for the absence of ethanol production plants in these regions. A crucial milestone to reaching this goal will be the optimization of technological aspects of converting MSW's cellulose fraction into ethanol, with continued research to characterize the fiber content of the different fractions in order to optimize delignification processes and to reduce GHG emissions of the MSW-to-ethanol conversion process relative to biogas production. But the greater challenge will be developing an innovative waste-management approach to sort and pretreat the different fractions of municipal residues to be used as a renewable resource for the extraction of delignified biomass and its conversion to bioethanol. This new process of MSW transformation needs to be developed within a comprehensive management approach, the accomplishment of which, in several Mediterranean countries, will require facing the difficult emergency situation brought on by MSW disposal.

On the other hand, although the Mediterranean countries France, Turkey, Spain, Egypt and Italy hold great potential for bioethanol production from agricultural residues, several hurdles have to be overcome in order to make the large-scale use of residual biomass as an energy resource economical and technologically viable. The main constraints to be faced to optimize the use of residual biomass from agricultural sources for the production of bioethanol in the Mediterranean region include cost, distribution and availability of biomass resources in specific geographic regions, technological bottlenecks of feedstock processing, vulnerability to climate change and resulting uncertainties for the future of the

agricultural sector, social acceptance and public perception, and competition from the petroleum-based sector.

To move from fields to fuel tanks, several aspects affecting feedstock cost and including both geographical factors such as the biomass species, yield, location, climate, local economy, and the systems used to harvest, collect, pre-process, transport, and handle the material need to be considered [28]. Feedstock cost and availability will be the driving forces influencing the selection of ethanol production-plant sites, and these same factors will largely control the rate at which this industry grows [117].

Three main contributions to feedstock cost can be considered: (1) *Grower Payment*, i.e. payment to the grower, which includes appropriate production costs and all other expenses related to the biomass value standing on the stump or in the field; (2) *Efficiency/Capacity,* including all expenses related to the equipment necessary to move the feedstock from the production location to the ethanol production plant; (3) *Quality*, i.e. biomass cost adjustments based on composition, moisture, and particle size distribution. Supply system costs, expressed as *Efficiency/Capacity,* include all expenses associated with harvesting, collecting, storing, pre-processing, handling, and transporting biomass to the biorefinery, and vary according to biomass varieties, yield, climate, local economy, and the specific engineering systems used. Supply system costs face significant logistical and, more importantly, feedstock diversity challenges, which are mainly dependent on four major factors: feedstock type, variety, location, and the quantity of biomass passed through the supply system. These challenges prohibit the near-term establishment of a consistent and uniform biomass supply system. Therefore, the supply systems for ethanol production plants will need to be individually defined for each plant as regional biomass variations, cropping practices, and equipment require optimization for relatively small, local areas. Thus, ethanol processing shall be initiated in limited areas and will spread as feedstock production systems, based on advanced feedstock supply system technologies, begin supplying large enough quantities to enable their cost-effective replication [118]. Pioneer supply systems will start by using the currently available infrastructure and technologies and be individually designed for ethanol production plants using specific feedstock types and varieties based on local geographic conditions. As the industry develops and cost barriers are addressed, the supply systems will incorporate advanced technologies that will eliminate downstream diversity and provide uniform, tailored feedstock for multiple plants located in different regions [118].

As one of the main threats to the prospect of large-scale ethanol production from agricultural residues in the Mediterranean, this region's vulnerability to climate change introduces new uncertainties for the future of the agricultural sector. Potentially negative impacts of climate change on agriculture are expected, including increased water demand and periods of water deficit, increased pesticide requirements and crop damage, and fewer cropping opportunities [119–122]. In general, changes in atmospheric CO_2 levels and increases in temperature are changing the quality and composition of crops and grasslands, as well as the range of native/alien pests and diseases. Relevant effects on the growing season of agricultural crops and crop-yield variability have been observed and such events are projected to increase.

There is evidence that the length of the growing season of several agricultural crops has changed. A lengthening of the growing season was observed between 1975 and 2007 in central and southern Spain and in central Italy, due to a reduction in spring frost events or to a progressive delay in the start of autumn frosts. However at the southern latitudes, the trend is towards a shortening of the growing season [123]. Climate-change projections foresee a warming in all seasons and for all scenarios, but warming will be greater in western and southern Europe in the summer, where limited water availability and high-temperature stress in that season will hinder plant growth. Moreover, the shortening of the growing season in these regions will negatively affect the productive success of the crops [123]. In general, a shorter crop cycle is strongly correlated with lower yields, with non-optimal use of the available thermal energy, solar radiation and water resources. Adaptation of farm practices by selecting suitable varieties or adapting the crop calendar will be crucial to reducing or avoiding the negative impacts of crop-cycle shortening.

Climatic conditions are projected to become more erratic with an increase in the frequency of extreme events (floods, hurricanes, heat waves, severe droughts) [124]. Climate and its variability are largely responsible for variations in crop suitability and productivity. For the Mediterranean area, where climate vulnerability is high, several studies have found an increasing trend towards more intense precipitation and a decrease in total precipitation [125–127]. As a consequence of climatic change, such events are projected to increase in frequency and magnitude, and crop yields to become more variable. The effects of increasing mean daily temperatures on agricultural yield depend on their magnitude and geographic extent. With an increase in mean annual temperature of 2 °C, cereal yields are expected to increase, partly because of the fertilization effect of the increase in CO_2 [124]. However, an increase of 4 °C or more will shorten the crop cycle and the CO_2 effect will not compensate for the resulting loss of yield. Crop yields are also at risk from more intensive precipitation and prolonged periods of drought, particularly in areas bordering the Mediterranean Basin.

Many adaptation options are available to adjust agricultural practices to the changing climate, considering that several environmental and anthropogenic factors, such as soil fertility, crop varieties and farming practices, influence crop yields. However, these opportunities differ among regions. Adaptive management is required to help reduce the risks to agricultural yields from climate change, and to make better use of opportunities. Changes in farming practices and land management can act as risk-mitigating measures. Changes in planting dates and crop varieties, and shifts from rain-fed to irrigated conditions will be required.

Further research on the conversion process is crucial to expand the application of agricultural residues to ethanol production beyond the laboratory scale, developing the necessary biotechnologies. Cellulose-extraction procedures and fiber pretreatments need to be optimized as a function of feedstock to maximize the enzymatic hydrolysis and fermentation processes. Bridging this technological gap will allow optimizing ethanol yield from cereal residues and improving the use of more residues (from olive tree pruning, and tomato and grape processing), thus further increasing the potential ethanol production capacity.

10. Concluding remarks

Demand for energy in the Mediterranean has more than doubled in the last 30 years, with an energy consumption of 990 Mtoe, accounting for about 9% of the world's energy demand, in 2005. Moreover, the energy demand in the Mediterranean is expected to continue increasing at an average rate of 1.5% per year, reaching up to 1426 Mtoe by 2030. The Mediterranean countries, particularly in the south, have a huge potential for renewable energy, estimated at more than double the energy demand in the south and north of the Mediterranean until the year 2050 [6]. However, today, there is under-exploitation of biomass for biofuel production, biomass accounting for just 21% of the total renewable capacity which met just 7% of the Mediterranean energy demand in 2005. Huge efforts are therefore needed to promote the production and use of biofuels in the Mediterranean, in order to counteract the dramatic rise in heat-stress risk occurring in the region. The only plant for cellu-

losic ethanol production currently operating in the Mediterranean is a demonstration plant constructed by the company Abengoa Bioenergy (http://www.abengoabioenergy.com) in Salamanca for ethanol fuel production from wheat and barley straw. Identifying lignocellulosic residues as raw materials for effective large-scale production of bioethanol fuel in the Mediterranean is an urgent priority if the region's growing energy demands are to be met and the climate change effects there alleviated.

Cereal crop residues are the most abundant agricultural residues in France, Italy, Spain, Turkey and Egypt, where they can be considered potential raw materials for large-scale ethanol production. In these countries, a fraction (15%) of the cereal crop production is considered as residual agricultural biomass that can be recovered from the field and potentially used for ethanol production; this figure is well below the total amount of cereal residues (50%) accounting for needs related to soil conservation, livestock feed and factors such as seasonal variation. From these residues, a potential production capacity of 8.5 Mtoe of ethanol can be expected, considering that based on current technologies, cellulosic biomass from crop residues has been shown to be readily converted to bioethanol at a rate of 300 l of ethanol produced per ton of biomass [63]. If the targets suggested by the Directive on the promotion of the use of biofuels and other renewable fuels for transport [33] are also considered for the Mediterranean, 25.87 Mtoe of biofuels (40.42 million tons of bioethanol) should be produced and used by 2010, corresponding to 5.75% of the expected Mediterranean oil demand in that year (450 Mtoe). From this perspective, the potential capacity of ethanol production from cereal residues would represent around 30% of the total Mediterranean biofuel demand. Olive tree pruning, and tomato and grape processing residues have also been shown to be abundantly produced wastes that do not currently have any market application in the Mediterranean region. Their effective transformation would allow a further increase in ethanol production by 4.6 Mtoe, thus achieving around 50% of the expected biofuel production capacity (Directive 2003/30/EC). However, the prospect of large-scale ethanol production from agricultural residues in the Mediterranean is threatened by many constraints. Limitations concerning cost, distribution and availability of biomass resources in specific geographical regions and vulnerability of the Mediterranean to climate change have to be faced within a systematic approach specifically conceived for the different varieties and specific regions.

Moreover, due to the lack of sufficient amounts of agricultural biomass in all of the other Mediterranean countries, MSW has been identified as an additional potential raw material, considering the vast amounts (180 million tons) of waste currently produced annually in the Mediterranean, and the fact that its management, collection, treatment and/or disposal has become a major problem throughout the Mediterranean region. Technological development of ethanol production processes from MSW is still in its infancy. Whereas on the one hand, ethanol production from MSW shows environmental and economic benefits relative to its production from other sources, further improvements are needed to reduce its GHG emissions with respect to its use for biogas production. As cellulosic ethanol technologies progress, the Mediterranean could use the cellulosic content of MSW as a transportation fuel feedstock – with a potential production capacity ranging from 17 (21 Mtoe) to 25 (30 Mtoe) billion liters – and simultaneously reduce externalities associated with waste disposal. However, the medium-term prospects for large-scale ethanol production from MSW in the Mediterranean require the development of an innovative waste-management approach that can offer a solution to the problem of MSW management, which is currently raising political, environmental and economic concerns in several Mediterranean countries.

To overcome the great bottlenecks for a renewable energy-based future in the Mediterranean, an integrated strategy based on strengthened regional cooperation needs to be adopted. Crucial steps in this strategy will include enhancing research and development cooperation, increasing investment in renewable energy, developing education and training programs, implementing encouraging policies and legislation, and working to drive the private sector to invest in renewable energy sources [6].

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